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REDUCED ENERGY BINDER FOR ENERGETIC COMPOSITIONS BACKGROUND OF THE INVENTION

I. Field of the Invention

The present invention relates generally to energetic compositions or formulations, particularly solid high energy compositions including propellants, explosives, gas generators and the like. More particularly, the invention focuses on improvements for reducing hazards sensitivity and product cost in propellant compositions.

The hazards sensitivity is reduced by substantially reducing the required relative amount of shock sensitive energetic plasticizers, particularly nitrate esters, such as nitroglycerin (NG), by replacing the conventional binder polymer and part of the plasticizer with a binder polymer more easily plasticized.

One important aspect of the invention focuses on the discovery that amounts of relatively high molecular weight polyester prepolymers, particularly polyester polyols, can be combined successfully with surprisingly low levels of energetic plasticizers (particularly nitrate esters) energetic compositions that are relatively low cost and characterized by comparable or superior mechanical properties. A preferred binder polymer is an isocyanatehigh molecular weight polyester diol poly(1,4butanediol adipate) or poly(tetramethylene adipate) (PTMA). The invention also enables improved formulae in which high cost, relatively sensitive, high energy, energy adjustment compounds, such as cyclic nitramines of fine particle size, including cyclotrimethylene trinitramine (RDX) cyclotetramethylene tetranitramine (commonly referred to as HMX) can be, if desired, partially or completely replaced by aluminum and ammonium perchlorate (AP) oxidizer and/or other combinations of particulate solids. Such cyclic nitramines of fine particle size are typically used to increase the energetic performance and to improve the mechanical properties of the composition.

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II. Relat d Art

Solid, high energy compositions such as rocket propellants, gas generators, explosives, and the like, generally contain particulate solids in the form oxidizers, fuels, burning rate modifiers, solid explosives, etc., dispersed in elastomeric binders. The elastomeric binders themselves may contain inert polymer materials, but these compositions may also contain high energy, hazards sensitive plasticizers, such as nitrate esters. plasticizing materials are known to enhance the mechanical properties as well as the energy output of the overall composition. The typical ratio, by weight of plasticizer to total polymer (including prepolymers, crosslinkers and curatives) in binder materials (commonly known as the P1:Po ratio) is about 2-4, i.e., 2 to 4 parts of energetic plasticizer to one part of polymer in the binder.

Recently, more stringent requirements imposed for lower hazards sensitivity have led to an increased demand for lower energy, but not entirely inert, binders which have become known as reduced energy or intermediate energy binders. The general approach to developing these binders has been to replace or dilute very high energy plasticizers with lower energy plasticizers while holding the Pl:Po ratio substantially constant at about 2-4.

An alternative approach to this problem which seemed logical was to simply dilute the high energy plasticizers with additional binder polymer material to reduce the overall binder energy as this would provide a more dense polymeric network which, in turn, would be expected to be a great deal tougher and more resistant to physical damage, critical another consideration for reducing sensitivity. It was found, however, that at the resultant lower Pl:Po ratios, the lower fraction of plasticizer was insufficient to properly plasticize the binder polymer and this resulted in unsatisfactory mechanical properties, especially with regard to low elongation. Thus, there has remained a need to solve the problem of fully plasticizing the binder polymer at lower Pl:Po ratios to reduce hazards

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sensitivity in a manner which preserves good mechanical properties or even enables improvements in mechanical properties.

Crosslinked binders disclosed by Baczuk et al (U.S. Patent 4,386,978) include urethane rubber materials that include certain polyester diols which contain both aliphatic and aromatic ester functions. These are combined poly-functional isocyanate having NCO an (isocyanate) functionality of at least 3. Energetic plasticizers are not reduced, however.

Godsey et al (U.S. Patent 5,468,311) discloses a composition having a binder system that includes polyols which may be polyesters or polyethers having a molecular weight from about 400 to about 4,000 and hydroxyl functionalities from about 2.0 to about 2.8. The preferred polyol is polyethylene glycol adipate. The preferred molecular weight range is from about 2,000 to about 3,000. A further patent to Godsey (U.S. Patent 4,298,411) depicts a propellant system that includes a pre-polymer of a hydroxy-terminated polyester and an isocyanate used in very small amounts as a crosslinking agent.

In U. S. Patent 4,775,432 to Kolonko et al, it has further been proposed to use relatively high molecular weight poly(caprolactone) polymers in propellant binders. Those formulae, however, require a ratio of plasticizer to binder that is at least 2.0:1 and preferably at least 2.5:1.

Whereas each of the above references addresses certain previous drawbacks in the art, none predict a low cost, reduced hazards energetic formulation with desired mechanical properties.

Accordingly, it is a primary object of this invention to provide an improved binder system for energetic compositions which maintains excellent mechanical properties, together with reduced hazards sensitivity.

A further object of the invention is to replace an amount of energetic plasticizers in binders for energetic

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compositions with binder polymers without sacrificing good mechanical properties.

It is another object of this invention to provide an improved binder system for high energy compositions using high molecular weight polyester prepolymers combined with a relatively low level of energetic plasticizer.

Yet another object of this invention is to provide lower cost energetic compositions of reduced hazards sensitivity and desirable mechanical characteristics.

A still further object of this invention is to provide an improved binder system for high energy compositions utilizing isocyanate crosslinked or cured, relatively high molecular weight PTMA pre-polymer as the binder polymer.

Yet still another object of the invention is to provide lower cost energetic materials by replacing part or all of the RDX or HMX fraction with a suitable solid material combination such as AP and aluminum.

Other objects and advantages will become apparent to those skilled in the art upon becoming familiar with the descriptions and accounts contained herein together with the appended claims.

SUMMARY OF THE INVENTION

The present invention overcomes many drawbacks in prior energetic compositions by the provision of improved reduced energy binder compositions for solid, high energy formulations including propellants, explosives, and related materials, generators together with formulations using these binders. The binders of the invention are particularly advantageous because they are relatively low cost and exhibit improved hazards properties relative to similar, higher energy binders. In addition, the binders promote excellent mechanical properties which allow additional composition variation leeway which, in turn, can be used to reduce cost and hazards sensitivity still further. The excellent mechanical properties survive in the formulations even without the reinforcement of fine particle size nitramines such as HMX and RDX.

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The binders are useful with any commonly used solid energetic species and successfully employ binder polymer materials to replace at least part of the energetic plasticizers thereby reducing the levels of energetic plasticizers, particularly nitrate esters, required in the binder. The binder system of the invention succeeds mechanically at levels of energetic plasticizers that are quite low.

The invention accomplishes the foregoing advantages by providing unique binder compositions that employ a cured high molecular weight polyester matrix, particularly polyester polyols which readily undergo crosslinking curing through active hydroxyl group sites using polyisocyanates in combinations with relatively low levels of energetic plasticizers. The preferred embodiment uses high molecular weight poly(tetramethylene adipate) or PTMA with NG, but other energetic plasticizers such as n-butyl-2-nitratoethyl nitramine (Bunena), trimethylolethane trinitrate (TMETN), triethyleneglycol dinitrate (TEGDN), butanetriol trinitrate (BTTN) and other materials also function effectively.

The polyester prepolymer materials of the invention are compounds that are readily plasticized by energetic plasticizers including nitrate ester compounds such that the relative level of high energy plasticizer can be reduced significantly. The formulas make use of material that is sufficiently plasticized at low Pl:Po ratios of about 1.0 such that lower hazards sensitivity advantages associated with the higher relative polymer levels can be It has been found, for example, that PTMA of a rather high molecular weight (MW ~ 6,000 in which the MW is a number average molecular weight) works extremely well. When used with NG at an approximate ratio of 1:1, or even slightly less, the polymer is sufficiently plasticized to enable excellent or superior mechanical properties to be realized.

While the detailed description focuses on the use of PTMA, it is believed that other high molecular weight

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polyester polyol materials having sufficient reactive hydroxyl group sites to react with a crosslinking agent, particularly a polyisocyanate, to form a cured polymer matrix may behave similarly. Thus, linear and moderately branched polyester polyols derived from aliphatic and/or aromatic starting materials, or from polymerizable lactones or mixtures thereof of sufficient molecular weight may function in a similar manner. Examples of other such compounds poly(1,4-butanediol include azelate), poly(diethyleneglycol adipate), poly(1,6-hexanediol adipate), poly(1,3-butanediol adipate), etc.

The present invention also provides reduced or intermediate energy binder propellant systems of reduced cost and reduced hazards sensitivity which maintain superior mechanical properties. Some formulas reduce both cost and hazards sensitivity by reducing or eliminating RDX or HMX and further reduce hazards sensitivity by utilizing novel, reduced energy binders. In this manner, it has been found, for example, that some or all of the high priced components RDX or HMX can be replaced by less expensive AP oxidizer and aluminum or other solids combinations.

In one example, a 75% solids propellant was prepared which utilized 53% unground (200μ) ammonium perchlorate and 22% aluminum (30μ) . That formula also contained 11.3% PTMA of MW approximately 6,200 and 12.19% NG. The propellant gave outstanding mechanical properties and less than 69 cards in NOL card gap testing.

According to the invention, it has also been found that a combination of plasticizers may be used in such formulas including amounts of inert materials to provide further flexibility in formulating useful mixes. An example of such an inert plasticizer is triacetin (TA) or triacetyl glycerine. The use of amounts of inert plasticizer allows a further reduction in the required amount of energetic plasticizer. The percentage of inert plasticizer used may vary greatly in the binder, which itself may vary greatly in the mix. One successful formula

used about 2.5% TA and another about 1.4% TA.

As a general comment with respect to many of the ingredients used in the several exemplary formulae disclosed herein, the following is a partial list of ingredient functions in the energetic compositions:

NC - crosslinker

PTMA - prepolymer

N-100, DDI, IPDI - isocyanate curatives

NG, TMETN, BuNENA, etc. - energetic plasticizers

10 TA - inert plasticizer

2-NDPA, MNA - stabilizers

AP - oxidizer, burn rate modifier

NaNO₃ - oxidizer, chloride scavenger

DCDA - burn rate suppressant

15 A1 - fuel

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TPB - cure catalyst

It is expected that a range of molecular weights for the PTMA binder material may be successfully used; however, it has been discovered that using molecular weights that are higher produces surprisingly superior results at low Pl:Po ratios. With PTMA, it is believed that the preferred range of molecular weights of PTMA begins above about 4,000 and preferably above 5,000, material of approximately 6,000 MW or greater is most preferred being found highly successful. The material has allowed the formulation of low-binder-energy propellant that requires no HMX or RDX and so can be made out of lower cost materials.

Another important advantageous characteristic of the binders of the invention is a relatively high electrical conductivity. This is also important with respect to reducing hazards by assisting in preventing the accumulation or buildup of large static charges in the associated energetic compositions.

DETAILED DESCRIPTION

The goals of the energetic formulae or compositions of the present invention are to reduce cost and reduce hazards

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sensitivities (hazards class 1.3) in energetic compositions including missile propellants. The energetic compositions of the invention use a binder system that includes a high molecular weight polyester polyol (polyester prepolymer) binder polymer and an energetic plasticizer. invention is based, at least in part, on the discovery that molecular certain higher weight polyols (polyester prepolymer) binder compounds are plasticized in the cured state much more readily than expected by energetic plasticizers to enable the Pl:Po to be reduced to just above 1.0 or even less. These compounds are particularly characterized by attached hydroxyl groups that provide reactive sites that react with crosslinking particularly isocyanates to form the cured polymeric matrix. While the examples of the detailed description particularly disclose PTMA, this is intended to interpreted as illustrative rather than limiting and many other polyester polyol-type compounds including linear and moderately branched hydroxyl polyester compounds derived from aliphatic and/or aromatic starting materials or from polymerizable lactones may work successfully. In addition, high priced, solid, energy enhancement ingredients such as nitramines including RDX and HMX can be replaced in whole or in part by solid materials such as Al and AP or possibly sodium nitrate (NaNO3).

Thus, the improvement achieved with the present reduced-binder-energy compositions is two-fold: (1) they can be used to reduce hazards sensitivity and cost by enabling partial or total replacement of RDX, HMX, etc., with AP, Al, and/or other solids and (2) they further reduce hazards sensitivity by providing binders that dramatically reduce the required relative amount of energetic plasticizer enabling replacement of some of the energetic plasticizer (NG, TMETN, BunENA, etc.) with polymer.

As indicated, poly(1,4-butanediol adipate) or poly(tetramethylene adipate) (PTMA) is the most preferred

binder polymer and it may also be identified by Chemical Abstracts Service (CAS) Registry Number 25103-87-1. In accordance with the invention, the required amount of high energy plasticizer such as energetic nitrate esters, particularly NG, can be reduced significantly while attaining as good or even superior mechanical properties. It will be understood that while detailed embodiments described herein are solid propellants typically used as rocket propellants, these are meant by way of example only and are in no way intended to limit the scope of application of the binder materials of the invention.

EXAMPLE 1

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A baseline reduced-binder-energy propellant used a 0 cal/g (binder heat of explosion, HeX_B) PTMA/NG binder in a 75%-solids propellant shown to give outstanding mechanical properties. That particular formula used all unground 200 μ AP. This formulation is shown in Table I. One-pint-mix properties of this formulation are shown in Table II. Such a formula is suitable for strategic missile propulsion, for example.

This formula is successful in accordance with a preferred embodiment of the invention. High molecular weight (6,000 or higher) PTMA has been found to become sufficiently plasticized at very low P1:Po ratios (approximately 1:1).

TABLE I

	Baseline reduced-binder-energy formulation				
	Ingredient	Weight %			
	RS 5 sec NC	0.06	Percent Solids	75	
5	PTMA 6000	11.30	P1:Po	0.99	
	N-100	0.97	Hex _B (cal/g)	0	
	NG	12.19	NC/PTMA	0.005	
	2-NDPA	0.12	NCO/OH	1.3	
	(2-nitrodiphenylamine)				
10	MNA	0.36	theor. I ⁰ _{sps} (lb _f s/lb _m)	260.4	
	(N-methyl-p-nitroaniline)				
	AP (200μ)	53.00	theor. p (g/cc)	1.84	
	Al (30µ)	22.00	theor. flame T (°K)	3756	
	TPB	(0.01)			

TABLE II

	One-pint-mix properties of baseline reduced-binder-energy			
	formulation (using all 200µ AP, except as noted).			
5	Tensile properties @ 2	in/min, 77	°F	
10	σ_{m} (psi) 84 ϵ_{m} (%) 244 ϵ_{r} (%) 244 ϵ_{0} (psi) 1610			
	120°F viscosity (kP)			
	$\begin{array}{ccc} \eta_{0.36} & 7 \\ \eta_{0.008} & 12 \end{array}$			
	120°F pot life (hr)	~27-36		
15	Ballistic properties (w	ith 50/50	90μ/200μ AP)	
:	70-g motor r ₁₀₀₀ (in/s 70-g motor n)	0.41 0.3	
	CIV (ft/s) 806			
	NOL card gap			
20	1 no-go at 69 car	ds		
	Hazards sensitivity			
		uncured	cured	
25	impact (cm)	6.9	21	
	friction (lb _f @ ft/s)	40 @ 8	100 @ 8	
	ESD (J)	0.15	0.26	
	FJAI (°C)	>300	>300	

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The viscosity of this propellant of 7 kP/12 kP (at $0.36~\rm s^{-1}/0.008~\rm s^{-1}$ shear rates) indicates that it would be easily processible in full-scale mixes. The pot life of approximately 27-36 hours is similar to that of current propellants used in rocket motors requiring multiple full-scale castings.

At 2 in/min, 77°F, the baseline reduced-binder-energy propellant gave $\sigma_m/\epsilon_m/\epsilon_r/E_0$ values of 84 psi/244%/244%/1610 psi (one-pint mix); where σ_m is tensile strength; ϵ_m is elongation at maximum stress; ϵ_r is elongation at rupture and E_0 is the initial tangent modulus. These properties were tested using JANNAF Class C tensile specimens. Although the abnormally high modulus should not present problems, additional one-pint mixes were made using a diisocyanate, isophorone diisocyanate (IPDI), with N-100 to reduce modulus and achieve even higher elongation. approach proved to be effective: $\sigma_m/\varepsilon_m/\varepsilon_r/E_0$ values at 2 in/min, 77° F went to 113 psi/414%/414%/1280 psi with 80:20 (isocyanate equivalents) N-100: IPDI, psi/455%/457%/900 psi with 60:40 N-100:IPDI.

CIV (critical impact velocity) testing, to determine material toughness, was performed on the baseline reduced-binder-energy propellant. The result was 806 ft/s (similar to Trident I C-4 propellants VRP and VTG-5A), indicating low friability.

The appearance of the burning aluminum particles (small, bright) in the microwindow bomb has indicated high combustion efficiency in the reduced-binder-energy propellant. 70-gram motors gave a burn rate at 1000 psi of 0.41 in/s which was higher than predicted by a propellant burn rate model (but this was an empirical model based on HMX-loaded propellants with lower levels of AP). The low slope of 0.3 was not unexpected at this high AP level. This propellant, with 53% AP, should be widely tailorable to adjust burn rate.

EXAMPLE 2

Another binder produced outstanding mechanical

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properties in an 84%-solids, low hazards (-850 cal/g Hex,) propellant containing 55% coarse (400 μ and 200 μ) AP and no This binder also used 6000 molecular bonding agents. weight PTMA. The primary plasticizer in this binder was BuNENA [the BuNENA was diluted slightly (~1:5) with an inert co-plasticizer, TA] and the Pl:Po ratio was 1.0. Although modulus was very high (2530 psi), σ_m and ϵ_m values were also extremely high for a propellant with an energetic binder and such a high level of such coarse solids -- 104 psi and 174%, respectively @ 2 ipm, 77°F. Properties were demonstrated and verified using a one-pint mixer. This example is also shown in Table III and in Table IV.

This example indicates that relatively small amounts of a variety of energetic plasticizers probably will successfully plasticize high molecular weight PTMA including plasticizers such as triethyleneglycol dinitrate (TEGDN) and butanetriol trinitrate (BTTN) and others.

TABLE III

	Reduced-binder-energy f	ormulation	with BuNENA/TA plastici	zer
	Ingredient	Weight %		
	RS 5 sec NC	0.04	Percent Solids	84
5	PTMA 6000	7.23	P1:Po	1.00
	N-100	0.62	Hex _B (cal/g)	-850
	BUNENA	6.47	NC/PTMA	0.005
	TA	1.41	исо/он	1.3
	MNA	0.23	theor. I^0_{sps} (lb _f s/lb _m)	261.0
10	ΑΡ (20μ)	5	theor. p (g/cc)	1.85
	AP (200μ)	20	theor. flame T (°K)	3712
	AP (400μ)	35		
	Al (30µ)	22		
15	DCDA (dicyandiamide) $(<10\mu)$	2		
	ТРВ	(0.01)		

TABLE IV

	One-pint-mix properties of reduced-binder-energy formulation using BuNENA/TA plasticizer.			
5	Tensile properties @ 2 in/min, 77°F			
10	σ _m (psi) ε _m (%) ε _r (%) Ε ₀ (psi)	104 174 176 2350		
	120°	F viscosity (kP)		
	៧០.36 ៧០.008	10 29		

TABLE V

15	Reduced-binder-energy formulation with mixed NG/TA plasticizer			
	Ingredient	Weight %		
	RS 5 sec NC	0.05	Percent Solids	75
	PTMA 6000	9.88	P1:Po	1.26
	N-100	0.67	Hex _B (cal/g)	-100
20	DDI (dimeryl diisocyanate)	0.26	NC/PTMA	0.005
	NG	11.24	NCO/OH	1.3
	TA	2.46	theor. I_{sps}^{0} ($lb_f s/lb_m$)	259.7
	2-NDPA	0.11	theor. p (g/cc)	1.83
25	MNA	0.33	theor. flame T (°K)	3728
	AP (20μ)	8		
	AP (400μ)	45		
	Al (30µ)	22		
-	ТРВ	(0.01)		

TABLE VI

	One-gallon-mix properties of reduced-binder-energy formulation			
	using mixed NG/TA plasticizer.			
5	Tensile properties @ 2 in/min, 77°F			
	o _m (psi)	79		
	ε _m (%)	350	ŀ	
	ε _r (%)	352		
10	E ₀ (psi)	799		
	120°F v	viscosity (kP)		
	n _{0.36}	3		
	η _{0.008}	5		
	120°F pot life (hr)	48		
Ballistic properties (one-pound motors)				
	r ₁₀₀₀ (in/s)	0.353		
	n	0.29		

EXAMPLE 3

Another propellant formula which produced excellent 20 mechanical properties is shown in Table V and the one-gallon-mix properties are shown in Table VI. This formula uses an amount of TA along with the NG as plasticizers.

EXAMPLE 4

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The formula of this example is shown in Table VII and illustrates a propellant formula that is plasticized with TMETN. This formulation also exhibits excellent mechanical and processing properties as shown in Table VIII.

EXAMPLE 5

The formula and mechanical properties of this example 30 can be seen in Tables IX and X, respectively. In this

example, a substantial fraction of the AP oxidizer has been replaced by $NaNO_3$. As with the mixes of previous examples, the mechanical and processing properties were excellent. This mix was also tested for volume resistivity.

5 TABLE VII

	Reduced-binder-energy	formulatio	on with TMETN plasticize	r
	Ingredient	Weight %		
	RS 5 sec NC	0.06	Percent Solids	75
	PTMA 6000	11.34	P1:Po	1.00
10	N-100	0.78	Hex_B (cal/g)	-260
	IPDI	0.11	NC/PTMA	0.005
	тмети	12.32	NCO/OH	1.3
	2-NDPA	0.03	theor. I^0_{sps} (lb _f s/lb _m)	261.0
	MNA	0.36	theor. ρ (g/cc)	1.82
15	AP (20μ)	10	theor. flame T (°K)	3663
	AP (200μ)	43		
	Al (30μ)	22		
	ТРВ	(0.01)		

TABLE VIII

	One-pint-mix properties of reduced-binder-energy formulation using TMETN plasticizer.		
5	Tensile properties @ 2 in/min, 77°F		
	σ _m (psi)	134	
	ε _m (%)	338	
	ε _r (%)	340	
10	E ₀ (psi)	1080	
	120°F visco	osity (kP)	
	ŋ _{0.36}	4	
	η _{0.008}	6	
	120°F pot life (hr)	50-53	

TABLE IX

	Reduced-binder-energy for	rmulation w	with AP, Al, and NaNO3 so	olids
	Ingredient	Weight %		
	RS 5 sec NC	0.06	Percent Solid	74.75
5	PTMA 6000	11.42	P1:Po	0.99
	N-100	0.98	Hex _B (cal/g)	0
	NG	12.31	NC/PTMA	0.005
	2-NDPA	0.12	NCO/OH	1.3
	MNA	0.36	theor. I_{sps}^{0} ($lb_f s/lb_m$)	245.7
10	AP (5μ)	13	theor. p (g/cc)	1.89
	AP (70μ)	17	theor. flame T (°K)	3732
	Al (30µ)	23		
	NaNO ₃ (<70μ)	21.75		
	ТРВ	(0.01)		

TABLE X

	One-gallon-mix properties of reduced-binder-energy		
	formulation using AP, Al, and NaNO3 solids.		
5	Tensile properties @ 2 in/min, 77°F		
	o _m (psi)	244	
	٤ _m (%)	394	
	ε _r (%)	394	
10	E ₀ (psi)	1570	
	120°F visco	sity (kP)	
	η _{0.36}	7	
	η _{0.008}	23	
	120°F pot life (hr)	>35	
15	volume resistivity (ohm-cm)	1 x 10 ⁸	

This invention has been described herein in considerable detail in order to comply with the Patent Statutes and to provide those skilled in the art with the information needed to apply the novel principles and to construct and use embodiments as required. However, it is to be understood that the invention can be carried out by specifically different formulas and devices and that various modifications can be accomplished without departing from the scope of the invention itself.

25 What is claimed is:

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